

Interactive comment on “Dissolution of atmospheric cobalt and zinc in seawater” by C.-E. Thuróczy et al.

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Dear K. Suzuki and referees,

We thank the referees for their effort in reviewing and giving relevant comments on our manuscript entitled “Dissolution of atmospheric cobalt and zinc in seawater”. The referees pointed out the novelty of this work and its importance regarding ongoing studies. They are acknowledged for their constructive remarks and we are addressing here the responses accordingly.

As mentioned by the referees, especially the third referee, this work is the first experiment of this kind, hence it could not be compared to other work. This work pioneers in studying the dissolution of two trace metals, cobalt and zinc, from dusts in HNLC

C4511

seawater. Furthermore it was conducted using an open flow reactor that prevents from any saturation and re-precipitation. The dissolution reactor has only been used with fresh water so far. The results obtained from this pilot work open a very new field of experiments.

The choice of the dust type was made among many stored dust at the laboratory because they are representative of contrasted origin respectively crustal and anthropogenic. The chemical properties of the crustal (natural) dust were extensively studied in previous works (references listed in the manuscript). As mentioned by the third referee, coal dust (ash coal dust) emissions may dramatically increase and may become one of the major type of anthropogenic emission. However such discussion is not the purpose of this paper and would extend too much its length.

The title will be changed into “Dissolution of cobalt and zinc from natural and anthropogenic dusts in seawater”, according to the second referee.

Most of the typing errors in the text, figures and tables were caused by the conversion between French and English languages but also versions in spreadsheets and SigmaPlot. All these errors have been identified and corrected. We will also get help from a native English speaker for proof reading the manuscript.

Special attention was given to avoid any contamination especially by using clean room environments and associated cleaning and washing procedures for trace metals analyses. Blank measurements from all the bottles and from the reactor did not show any diffuse contamination.

Please note that the second referee made an erroneous comment on the first equation (EQ.1) that we do not accept.

We will carefully take into consideration each of the remarks in order to proceed to the revision of the manuscript. Upon acceptance, a revised version will be sent.

Best regards

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1-Reply to Anonymous Referee #1

General comments

This paper is discussing the dissolution of cobalt and zinc from soil and coal dust particles into seawater, which was studied using an open-flow reactor. The dissolution of cobalt and zinc from aeolian dust is a key step to supply the bioavailable species to surface water in the open ocean. Since the process has not been studied well, the authors' data could be a potential contribution. However, this paper lacks critical information and preciseness for a standard scientific paper, and the discussion is not fully convincing. Thus, I cannot recommend it for publication in Biogeosciences.

We acknowledge that we do not extensively describe the system but we provided the relevant information to support our conclusions. In the revised version of the manuscript, we will further detail the sections which were not clear or precise enough. The ambition of this paper is not to put a final dot and solve all the problems related to solid-liquid chemical interactions.

Specific comments

- 1. Critical materials in this study are dust particles and seawater. However, the both materials are not sufficiently described.

What are the major components and minerals in your dust particles

The coal dust and natural loess are already described in the discussion part as well as in the publications we refer to:

“For instance the coal dusts were mainly constituted of spheres smaller than 1 μm with a fraction easily exchangeable (75%) and a carbonated structure (< 15%) (Guieu et al., 1997; Velay, 2006).”

“In opposite, particles from the natural soils were constituted of quartz, clay, feldspath and pyroxene, in which alumino-silicated mould represents 90% of the whole structure

C4514

(Ausset, 1996; Ausset et al., 1999, Velay, 2006).”

Mineralogy would bring valuable information on the dissolution processes, but it is rather complex and would deserve a specific study. Here the work is a first step towards understanding the dissolution of dust in seawater and comparing anthropogenic versus natural dust fates for Co and Zn. However, even if the elemental composition of the dusts used is reported in the references cited above, we will add here this information in a table.

You should evaluate the speciation of cobalt and zinc using a sequential extraction to discuss its effect on dissolution.

Such proposed experiments can be the subject of another scientific work. The present experiment is by itself already a kind of extraction experiment.

The characteristics of seawater are unclear. Which station and how many meters in depth was it taken from?

The seawater collected for this work is described in detail in the method section and the referred papers. We add the following details: “in the mixed layer depth at the chlorophyll maximum”:

“The seawater used for these experiments was collected in a HNLC area in the mixed layer depth at the chlorophyll maximum during the KEOPS cruise aboard RV Marion-Dufresne in 2005 (Blain et al., 2007) with ultra-clean conditions using a kevlar wire and GO-FLO bottles.”

Did you use homogenized seawater for all experiments?

In the method section:

“Twenty liters were filtered on board using 0.2 μm Sartorius Sartobran cartridge and stored in ultra-clean Nalgene bottles (LDPE) in the dark.”

We will add this detail: “The 20 L bottle was stirred before use.”

C4515

How many concentrations of cobalt and zinc did it contain?

These values are already given and referred as “background concentrations” in the method section.

We will just add: “background concentration ($[X]_{in}$)”.

“ $[X]_{in}$ ” described in the equations part.

Was the effect of dissolved organic matter and microorganisms negligible on the results?

A single bulk of 20 liters of seawater, 0.2 μm filtered water, kept in the dark and homogenized was used for all the experiments. If there was any effect of DOM, it was the same for each experiment. Because of the pore size of the filter, it is unlikely that microorganisms were present and therefore with no effect on the results.

- 2. Judging from the large error bars, I am worried that the authors measured very small variations in concentrations of cobalt and zinc. In this case, contamination during experiments could be serious. The results of the dissolution experiments are reported only in percentage, and the number of runs and the definition of error bars are not given. Thus, it is not possible to assess the significance of data. The authors should quantitatively show that the contamination is negligible and that their data are significant and reproducible.

Blanks were performed by running the dissolution reactor without any dust inside. Blanks were also performed with the sub-sampling bottles. No contamination was detected neither for Co nor Zn. We recall here that all these experiments and analyses were performed in clean rooms (ISO4 or 5) with ultra clean procedures and ultra clean material (including bottles, acids, water, . . .). We can add a table showing the concentrations found in blanks and experiments with associated uncertainty, but if possible as an annex to the paper.

To obtain quantities in nmol/min instead of %/min, the reader can multiply the

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percentage by the bulk composition of the selected dust.

The uncertainty plotted on the graphs is calculated from the uncertainty measured in the concentrations following uncertainty propagation in EQ.1 and 2 for the dissolution rate graphs. We will add a fourth equation (EQ.4) which will show how we calculate cumulated dissolution from dissolution rate. If only one experiment was done for each condition, replicates were made for the metals analyses. Analytical uncertainties are calculated by computing analytical replicates done for each sample.

Extensive explanation in the paper would be too long and is based on classical computation in analytical chemistry.

- 3. I cannot follow the equations 1-3 on pages 10889-10890. The authors should show the dimension for each term. I wonder if the first and second terms in eq 1 evaluate the same quantity in a different manner.

The statement "last term" is indeed imprecise and might have confused the referee. We should call it "second term of the right member in the equation". The two sides of the equation are of course equal. The dimensions for each term were also added in the text to make easier the understanding:

EQ.1 and 2:

"Where DR_X is the dissolution rate of the element X (mol/min), F the flow rate (mL/min), $[X]_{in}$ and $[X]_{out}$ the respective dissolved concentrations (mol/L) respectively at the input and the output of the dissolution reactor, V the volume of the dissolution cell (mL) and t the time (min)."

EQ.3

"mx is in mol"

The Table 2 will be modified to put the concentrations in $\mu\text{mol/g}$ instead of $\mu\text{g/g}$.

- 4. In Figures 2 and 3, the error bars for dissolution rate and solubility are very large.

C4517

Is the difference statistically significant between natural loess data in the dark and illuminated?

For the loess the difference between "illuminated" and "dark" Co is not significant in the dissolution rate graph (fig.2) but the cumulative solubility curve (fig.3) shows significant differences at the beginning of the experiment. This is due to a statistical effect because the dissolution rate for "illuminated" Co is systematically higher at the beginning of the dissolution experiment.

- 5. The values of cumulated solubility are not consistent between text on page 10890 and figure 3.

Corrected

- 6. The authors should discuss the reason for the dependency of cumulated solubility on square root of time. Its physicochemical meaning is not clear to me.

As explained in Wollast (1967), it shows "diffusion processes from an altered layer, presumably formed by rapid initial hydratation and exchange of H^+ for K^+ ."

In the discussion part:

"The square root shape obtained after 1 hour of dissolution indicates a continuous and stable weathering process for Co and Zn in the anthropogenic particles."

Technical corrections

- 1. Quantitative description is hoped in abstract as well as in text.

Corrected

-2. While Co shows correlation with nutrients in the upper water, the whole vertical profile of Co is generally different from that of nutrients.

We changed the description of the type of vertical profile for Co, as also mentioned by Referee#3:

C4518

“For instance the distribution of dissolved Zn in seawater shows nutrient-like profile (such as phosphate and silicate; Saito and Moffett, 2002a) whereas Co shows a hybrid-type profile combining nutrient-like and scavenged-like vertical distribution (Noble et al., 2008).”

- 3. *I do not understand that the detection limits are as low as 0.019 nM for Co and 0.14 nM for Zn, while the background concentrations are 0.049_0.02nM (n=4) for Co and 0.845_0.1nM (n=3) for Zn.*

The standard deviations of the background measurement were not well reported in the manuscript. Background concentrations in seawater corresponds to the concentration of Co and Zn naturally present ($[X]_{in}$). This water was used for dissolution experiments.

“The background concentrations measured by voltammetry in the seawater were 0.049 ± 0.007 nM for dissolved Co ($n = 4$) giving a detection limit of 0.021 nM for Co, and 0.845 ± 0.047 nM for zinc ($n = 3$) giving a detection limit of 0.142 nM for Zn.”

- 4. *The numbers of figures should be consistent throughout the paper. For example, “Figures 2 and 4” should be “Figures 2 and 5” in line 4 on page 10890. All figures should be referred in the text. For example, figure 5 is missing on page 10891.*

Corrected

- 5. *Why is the solubility at reaction time of 2 h regarded as typical?*

The choice of 2h for the dissolution experiments was limited by the volume of seawater available from a same container. This water was used for all the experiments (also for comparing the experiments) including rinsing and blank run for the reactor and calibration for the metal analysis by voltammetry. Moreover, using an open flow reactor means that there is no recirculation of seawater, so the volume needed for a complete experiment is large.

C4519

2-Reply to Anonymous Referee #2

10883: *The material used is not actually atmospheric dust so the title must be changed to something like “Dissolution of cobalt and zinc from model dusts in seawater”. Or “Dissolution of cobalt and zinc from Cape Verde soil and coal fly ash in seawater” The writing has very many small grammatical and language errors. A native English speaker should fix it.*

As mentioned in the letter above, we changed the title into: “Dissolution of cobalt and zinc from natural and anthropogenic dusts in seawater”.

10885: *carbonic anhydrase, not carboxyl anhydrase.*

Corrected

“Phytoplankton community structure” is more definitive than “structure of the phytoplankton assemblage.”

We agree with this statement therefore we corrected it.

19886: *The soil is sieved to <20 um, but what is the actual size distribution?*

We decided not to show the size distribution of the 2 dusts used for the work. However, all dust samples (coal dust, loess and other dusts) were sieved using different size fractions, as showed in the table below for the 2 dusts described in the manuscript.

Grain size separation (μm)

Saharan dust is about 1-3 um, so 20 um is very large by comparison, and much lower surface area to volume ratio. What impact does this have on the conclusions, and on the extrapolation of the results to actual atmospheric dust solubility?

The choice of <20 μm for the smallest fraction was partly due to the size of sieves available and the sieving method which must be dry sieving.

The fraction <20 μm of the loess is actually also constituted of grains much smaller

C4520

Size (μm)	Coal dust (%)	Loess (%)
> 500	0.2	0
250-500	0.4	0
150-250	3.6	3.7
80-150	20.6	14.7
63-80	3.3	7.1
40-63	25.1	27.9
20-40	44.2	45.6
< 20	2.1	0.5

than 20 μm as clearly seen on Fig.1 (Microscopy) where particles of all sizes are seen. This method is also commonly used to prepare large amount of aerosol like particles.

The soils were sieved through successive meshes (<20 μm to >500 μm). To be as representative as possible of the wind-transported material the fraction passing through the 40 μm and through 20 μm mesh were used for the determination of the elemental composition and the <20 μm for the dissolution experiments in open-flow reactor.

The soil has been probably exposed to very different conditions on the ground compared to actual aerosol dust. If it has rained, then the particle chemistry would have been completely altered. What is the history of the deposit where the soil was collected?

The samples collected were exposed to scarce rains at Sal Island. Crustal dusts from other locations are also influenced by rain and erosion before being transported by the wind in the atmosphere, thus they are comparable to our samples. We will add one more reference in the manuscript (Desboeufs et al. 1998, JGR).

Is the coal dust really “fly ash”, collected after the coal has been burned? If not, then the data from unburned coal is not at all relevant, and would have to be removed from the paper.

C4521

The coal dust is flying ashes collected in the electrostatic separators before exhaust. Combustion is almost complete.

“The second one, a coal dust, was flying ashes collected in electrostatic separators before exhaust in a power plant (le Havre, France), where combustion was almost completed. It was used for simulation of an anthropogenic aerosol.”

10889: *The two terms in Eqn.1 would yield the same flux, so adding them together yields a flux that is 2 times higher. How can an error of this magnitude be made? It implies that they did a very poor job of proofreading the paper, and casts doubt on the rest of the data and the interpretation.*

EQ.1 describes an open flow reactor. The first term of the right member is the dilution of the soluble element in the reaction cell from the dust; the second term is the dilution effect of the solution in the reaction cell by the new solution input. So, the equations EQ.1 and 2 are true and already validated many times by peer reviews in previous publications listed in the references.

“The reviewer seems to have done a poor job reading this paper”

10892: *The effects of particle size are mentioned, but surface area/volume ratios are not explicitly discussed. Isn't this the major factor, in addition to the different chemistry of the particles.*

The coal dust particles have indeed not the same surface than the loess particles. Size distribution is also not the same. We cannot conclude on the major factor which drives the dissolution rate, if it is the surface/volume ratio or the mineralogy or both.

From the discussion:

“Differences in the morphology of the dust could account for some of these dissolution features. Indeed based on solubility rates of spherical particles (using the Stokes-Einstein equation), the small spherical particles of coal dust should be more soluble than the particles of the loess (e.g., bigger and complexed shapes; Fig. 1), provided

C4522

the dissolution is proportional to the particles size. This would be the case indeed for Co; but not for Zn (Table 3)."

"For instance the coal dusts were mainly constituted of spheres smaller than 1 μm with a fraction easily exchangeable (75%) and a carbonated structure (< 15%) (Guieu et al., 1997; Velay, 2006)."

"In opposite, particles from the natural soils were constituted of quartz, clay, feldspath and pyroxene, in which alumino-silicated mould represents 90% of the whole structure (Ausset, 1996; Ausset et al., 1999, Velay, 2006)."

10893: *The reference to Fig 3 in line 3 should be Fig. 5, correct?*

Indeed, some table and figures numbers did not correspond. We corrected it.

10895: *These experiments are interesting, and the method for measuring solubility is cleaver, but it does not mimic the processes occurring when atmospheric aerosols are deposited to the ocean by wet or dry deposition. Wet deposition will pre-solubilize many trace elements in very dilute solutions that can sometimes be quite acidic. Wet deposition might account for more than 50% of total deposition. These experiments are not relevant to what might be the dominant mode of aerosol deposition to the oceans. Dry deposition will deliver aerosols to the air/sea interface, where the sea surface microlayer has high concentrations of organic lipid-like compounds, bacteria, etc. The initial exposure to the dust would be very different from what is done in these experiments with bulk seawater. How long will dry deposited dust sit in the microlayer, interacting with the organic compounds, etc. before they are mixed into the bulk solution? What are the mixing rates for small particles across the microlayer? What are the organic ligand concentrations in the bulk seawater, and are they allowed to interact with the model particles long enough? What are the implications of this on your conclusions?*

The remarks here are interesting; unfortunately we cannot answer to it in this pilot work (from our experiments). This opens a way for future experiments.

C4523

3-Reply to Referee #3, Mak Saito

We agree with all the comments of reviewer#3 and will include them in the revised version.

General Comments:

This manuscript present valuable dissolution data for cobalt and zinc from natural dust (Cape Verde) and finer anthropogenic coal dust into seawater using a novel flow through reactor and low level cobalt and zinc voltammetry techniques. The data look quite robust, and as the authors note this is some of the first data of its kind.

I would argue with the conclusions that their estimates suggest that the contribution of Co and Zn from dust is negligible. I think it is small, but not negligible as I describe below. Moreover, they do not make similar estimates for contributions from anthropogenic sources in more heavily polluted regions, saying data is unavailable. I think this is not necessarily true, and some simple estimates would be invaluable in knowing the relative import of their work here.

In general the manuscript could use some minor improvements in writing. I recommend accepting after suitable revisions.

Specific Comments:

The authors make the interpretation that Co and Zn contributions are negligible, adding 0.5 and 25pM respectively to a 50m mixed layer depth in a strong natural dust event. Yet both cobalt and zinc can be drawn down to very low picomoles/L values in surface waters, particularly in the remote regions of the Pacific (e.g. below 10pM for Co below 50pM for Zn is typical). Comparison of their estimates of dust flux with the Atlantic seawater concentration data is obviously a comparison with a region that receives far more aeolian deposition and hence might already be inclusive of the dust dissolution effects. Moreover, phytoplankton drawdown and subsequent remineralization processes of nutrients at these very low values can likely occur more quickly than homogenization

C4524

of water masses (and conservative tracers) within the mixed layer, creating observed nutrient-like depletion in 10's of meters. Hence short-term input to the upper 10 or 20m could begin to contribute 25% of existing Co inventory, and perhaps more than 100% of Zn inventory. This may not be enough to create broad surface maxima for Co (as for Al or Pb), but it is likely is a significant contributor to the upper water column inventory. I think the result that coal materials produce 5-fold more dissolved cobalt than loess is important. In regions that are heavily impacted by coal combustion, could this be a major cobalt source?

This could indeed be the case, but we have at the moment no scientific argument to state this hypothesis.

North America and Asian continents are both major coal combustion sources. Some estimates similar estimates to those presented for loess in Table 5 should be made and included. Given the projected large increases in coal combustion in this century, this is actually potentially quite an important calculation even if a rough estimate.

We can find accurate models and measurements for natural aeolian desert dust inputs to the oceans. But we have no data at the moment on the Co composition of anthropogenic dust and intensities of such emission. However, we could take emission factors for coal power plants and extrapolate very roughly the impact of coal combustion at a global scale. We think that this could be a very good job for modelers.

What would this mean for the relative abundances of cobalt and zinc in anthropogenically influenced areas? The potential ecological effects on phytoplankton composition of changing the Co:Zn ratio are also quite important as well, as the authors note. It seems that Zn dissolution is not higher in coal dust, but coal dust begins with 7 fold more Zn, so by quantity of Zn (as opposed to percentage dissolution) anthropogenic sources could be important as well.

Indeed, variations in natural and anthropogenic inputs between different locations can induce large variations in Co/Zn ratio in surface waters, thus having a potential impact

C4525

on the phytoplankton community structure. These details will be added in the discussion part.

Comments on other reviews:

Reviewer #1's concerns about contamination are overstated. Cobalt is not highly contamination prone, and cobalt analytical work typically suffers instead from reagent blank contamination, which the authors have constrained. The seawater background level of 49pM is reasonable, suggesting no contamination. The zinc seawater background level of 0.8nM is also reasonable for Southern Ocean waters (KEOPS). Zn contamination, which is extremely easy to do, would be obvious since it typically results in nanomolar concentrations. If anything, these experiments are remarkably clean given the complex manipulations involved and difficulty of working with Zn.

Reviewer #1's concern about seawater collection are also overstated: seawater collection was done under trace metal clean conditions, the material was filtered, and the cobalt and zinc background of that water was carefully measured.

The Reviewer #1's comments about organic complexes and microbes are important and valuable. However, given this is the first paper on the subject of Co and Zn dissolution, I think it is asking too much to expect additional experimentation regarding complexation and microbial processes. I think discussion of the potential complexation effects should be added (e.g. could there have been natural ligands that promoted some of the dissolution observed here etc.).

No analyses of the organic complexation have been performed in this work. It can be addressed as a general comment on effect of the organic complexation, but cannot be supported by new data.

Reviewer #2's comments about sources of dust are interesting, but again since this is the first focused study on Co and Zn solubility in seawater I do not think the publication of this data should be prevented because they did not also conduct prewetted

C4526

experiments. More information about the coal dust source would be useful.

We will add the details about this source as mentioned by referee#2.

Technical comments:

Dissolution %'s should be written into the abstract (Table 3 and 5)

Corrected

Cobalt and zinc are sometimes capitalized in the middle of sentences, change to lowercase.

Corrected

10884: Line 11 delete "in" change to "than natural particles"

Corrected

10884: Line 16 add "a", "oceans are a major source"

Corrected

10884: Cobalt is better classified as a hybrid-type profile combining nutrient like and scavenged-like vertical structure, see Noble et al. 2008.

Corrected

10885: Change activations to activity

Corrected

10885: Change carboxylic to carbonic

Corrected

10885: Change Doesn't to does not

Corrected

C4527

10886: dint?

Corrected, and now replaced by "using"

10886: is there any filtration of the material coming out of the reactor?

The dust particles introduced in the dissolution chamber were $<20 \mu\text{m}$. The pore size of the filter placed at the exit of the reactor was $0.4 \mu\text{m}$. Therefore the fraction passing through the filter is dissolved.

10886: Does the first time point contain the very first sample out of the reactor, e.g. any chance for a large spike that is missed by this design?

Yes, the first time point contains the very first water sample. It was obtained only 4minutes (time to fill the reactor) after the dust was in contact with the seawater. The first time-sample did not always have the highest concentration in Co or Zn. For the coal dust, Co and Zn first time-point were high and followed by a quick decrease with time, while for the loess, low concentrations of Co and Zn were measured at the beginning, followed by a first maximum at 10-20minutes then low concentrations again before a continuous increase after 1h.

10890: line 7 "Sensible" replace with significant or clear.

Corrected, replaced "sensible" by "no clear"

10890: line 14: awkward sentence, rewrite

Corrected

10890: line 25: replace anymore with thereafter

Corrected

10891: line 5:10 times

Corrected

C4528

10891: line 10 give Fig #.

Corrected

10891: line 19: zinc

Corrected

10892: line 20, figure 3 is a cobalt figure, correct fig #, also 10893, line 2.

Corrected, changed into figure 5

10892: line 25: complexation processes: discuss in more detail in the paper

See here above comment.

10893 line 16 input

Corrected

10893 line 20-23: where is the % given? Not in table 2,3? Table 3 caption is unclear.

The percentages are given in table 3.

Table 2 shows the elemental composition of the dusts (concentrations of Co and Zn in ppm), whereas table 3 shows the total percentage of metal dissolved after 2h (related to the initial composition).

The caption of Table 3 is now changed into: "Percentage of dissolved metal from the initial composition (*cf.* Table 2) of the dust after 2h of dissolution in seawater."

This calculation should be done for coal dust as well.

See here above comment.

10893 line 28: *From what I have seen in cobalt profiles from around the world, I would argue they are small but likely significant sources.*

We agree with this remark therefore we will change this statement into: "The Co inputs

C4529

to the mixed layer calculated here (e.g., 0.01 to 0.50 pM) are thus small compared to the concentrations found in the North Atlantic, as well as for the Zn inputs (0.43 to 25.06 pM) but these inputs are likely to be significant sources."

10894 line 10 change to "provided"

Corrected

10895 line 10: where no extrapolation

Corrected

10895 line 11: *awkward sentence. Replace with something like: Characterization of Co and Zn dissolution from natural and anthropogenic particles into seawater has not been previously reported to our knowledge.*

Corrected

10895 line 15 *awkward: quickly but less. Change to "released Zn quickly, but the quantity was less than..."*

Corrected

Interactive comment on Biogeosciences Discuss., 6, 10883, 2009.

C4530